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(71) Applicant (for all designated States except US): ALUMI-PLATE INCORPORATED [US/US]; 8960 Springbrook Drive, Minneapolis, MN 55433 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): FISCHER, Juergen, K., S. [DE/US]; 8960 Springbrook Drive, Minneapolis, MN 55433 (US).

(74) Agents: DAIGNAULT, Ronald, A. et al.; Merchant & Gould P.C., P.O. Box 2903, Minneapolis, MN 55402-0903 (US).

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(54) Title: ALUMINIUM ELECTROPLATING FORMULATIONS

(57) Abstract: Electroplating electrolyte compositions including $CA \cdot (nAl(C_3H_7)_3(2-n)AlR_3)$ where n is 0 and less than or equal to 2; C is Li, Na, K, Rb, Cs, NR⁴, or mixtures thereof wherein R' is H, CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof; A is H, F, Cl, Br, or mixtures thereof; R is H, halogen, CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof; and an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof are described. Aluminum and magnesium/aluminum electroplating compositions including $C \cdot (nAl(C_3H_7)_4(1-n)AlR_4)$ where n is 0 and less than or equal to 1, where C is a cation such as, Li, Na, K, Rb, Cs, or mixtures thereof; R is H or an alkyl such as, CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof are also described. The aluminum and magnesium/aluminum electroplating compositions formulation can include a solvent such as, an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof.

ALUMINIUM ELECTROPLATING FORMULATIONS

This application is being filed as a PCT international patent application in the name of ALUMIPLATE INCORPORATED, a U.S. corporation, on 30 April 2002, 5 designating all countries except the U.S.

Background of the Invention

The invention relates generally to the field of electroplating and more specifically to aluminum and magnesium/aluminum electroplating.

10 The science of electroplating has been developed over a number of years, beginning perhaps with Ziegler et al., U.S. Patent No. 2,849,349. This patent is hereby incorporated in its entirety by reference herein. Lehmkuhl et al., U.S. Patent Nos. 5,007,991 and 5,091,063, and Birkle et al., U.S. Patent No. 4,417,954 likewise are incorporated in their entirety by reference herein.

15 While electroplating is not a new art, possible advances remain. Areas of possible improvement include, for example, throwing power and current density. Throwing power refers to the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped object. Current density refers to the electrical current (amp/dm²) that can be applied across the anode and the cathode during the 20 electroplating process.

Summary of the Invention

Aluminum electroplating electrolyte compositions include CA•(nAl(C₃H₇)₃(2-n)AIR₃) where n is greater than 0 and less than or equal to 2; C is Li, Na, K, Rb, Cs, 25 NR⁴, or mixtures thereof wherein R' is H, C₁-C₈ alkyl, e.g., CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof; A is H, F, Cl, Br, or mixtures thereof; R is H, C₁-C₈ alkyl, e.g., CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof; and an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof.

30 The above aluminum electrolyte composition of the above-identified formula also includes embodiments where n is from 0 to 2 when such aluminum electrolyte compositions are in admixture with other aluminum alkyls, ethers, alkoxy-aluminum alkyls, aluminoxanes, or mixtures thereof.

Aluminum and magnesium/aluminum electroplating compositions include $C \cdot (nAl(C_3H_7)_4(1-n)AlR_4)$ where n is from 0 to 1. C is a cation such as, Li, Na, K, Rb, Cs, or mixtures thereof. R is H or an alkyl such as, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , or mixtures thereof. The aluminum magnesium/aluminum electroplating compositions formulation can include a solvent such as, an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof.

Brief Description of the Drawings

Fig. 1 is a flow diagram of an electroplating process.

10 Fig. 2 is a flow diagram of a pre-treatment process shown as box 100 in Fig. 1.

Fig. 3 is a flow diagram of the pre-treatment process shown in Fig. 2 where a plasma etch is used.

Fig. 4 is a flow diagram of a blower system for an electroplating process.

15 Fig. 5 is a schematic of a bulk plating device for an electroplating process.

Detailed Description

The term "about" is presumed to modify all numeric values, whether or not explicitly indicated. The term "about" generally refers to a range of numbers that one of skill in the art would consider equivalent to the recited value (i.e., having the same function or result). In many instances, the term "about" may include numbers that are rounded to the nearest significant figure.

The term "M" is molar amount commonly used in chemistry. The formulation examples and claims report values for concentrations in mol per mol salt or mol per mol cation.

25 Fig. 1 is a flow diagram of an electroplating process. A base metal enters the electroplating process 10 at a pre-treatment step 100. The base metal can be any material that can be plated with aluminum, magnesium, aluminum/magnesium or the like. The pre-treatment step prepares the base metal for plating by removing any non-base metal impurities from the base metal. The pre-treated base metal proceeds to a 30 plating process 120. The plating process 120 plates the base metal with aluminum, magnesium, aluminum/magnesium or the like. The plated base metal proceeds to a post-treatment process 130. The post-treatment process 130 prepares the plated base metal for further process such as, for example, drying, application of conversion

coatings, lubrication, sealers and the like. The pre-treatment, plating and post-treatment processes can take place in an inert atmosphere or under vacuum.

Pre-treatment

5 Pre-treatment provides a clean surface on the piece or base metal to be coated. To remove fat, oxides, and other impurities from the surface, degreasing, etching, and/or descaling operations are carried out. Each treatment step is followed by one or more rinsing steps and conducted in such a manner as to minimize loss and to recycle valuable material.

10 Fig. 2 is a flow diagram of a pre-treatment process shown as box 100 in Fig. 1. The base metal enters the pre-treatment process 201 at degreasing 200. Degreasing 200 removes grease and the like from the base metal. Degreasing solutions can include surfactants or other degreasing materials. The degreased base metal proceeds to a water rinse 205. The water rinse 205 removes the degreasing solution from the degreased base metal.

15 The rinsed and degreased base metal proceeds to an electrolytic degreasing 210 to further degrease the base metal. The further degreased base metal proceeds to a water rinse 212. The further degreased and rinsed base metal proceeds to an acid etch 215 to remove oxides from the base metal. The acid may be any acid capable of 20 removing oxides from the base metal. The acid etched base metal proceeds to a water rinse 220 to remove any remaining acid from the base metal.

20 The etched base metal then can be nickel plated 225. The nickel plating thickness can be 2 micrometers. The nickel plated base metal can be water rinsed 230 and dried 235.

25 The dried nickel-plated base metal enters an air lock 240 and vacuum environment. The plated base metal proceeds to an activation bath 245. The activation bath 245 can include an aqueous inorganic acid in aliphatic mono- or di- or tri-hydric alcohol. The inorganic acid may be hydrofluoric acid and the alcohol can be ethylene glycol, for example. The composition of the activation bath 245 must be 30 compatible with the base metal.

20 The activated base metal proceeds to an intermediate rinse 250. The intermediate rinse 250 includes a material that is soluble with the later electrolyte solvent. The intermediate rinse 250 can be an aliphatic alcohol such as, for example,

diethylene glycol monomethyl ether or a mixture of the electrolyte solvent with an aliphatic alcohol such as, for example, toluene and di-ethylene glycol monomethyl ether.

A first electrolyte solvent rinse 255 removes remaining intermediate rinse material. The first electrolyte solvent rinse 255 can include up to 10% of the aliphatic alcohol used in the intermediate rinse as impurity. A second electrolyte solvent rinse 260 further removes intermediate rinse material. The second electrolyte solvent rinse 260 can include up to 1% of the aliphatic alcohol used in the intermediate rinse as impurity. A third electrolyte solvent rinse 265 further removes intermediate rinse material. The third electrolyte solvent rinse 265 can include up to 0.1% of the aliphatic alcohol used in the intermediate rinse as impurity.

The base metal rinsed with the electrolyte solvent can proceed to an electroplating process 270.

15 **Plasma Etch Pre-Treatment**

Fig. 3 is a flow diagram of the pre-treatment process shown in Fig. 2 where a plasma etch is used to remove impurities from greasy and heavily oxidized base metal.

The base metal enters the pre-treatment process 301 at degreasing 300. Degreasing 300 removes grease and the like from the base metal. Degreasing solutions can include surfactants or other degreasing materials. The degreased base metal proceeds to a water rinse 305. The water rinse 305 removes the degreasing solution from the degreased base metal.

The rinsed and degreased base metal proceeds to an electrolytic degreasing 310 to further degrease the base metal. The further degreased base metal proceeds to a water rinse 312. The further degreased and rinsed base metal proceeds to an acid etch 315 to remove oxides from the base metal. The acid may be any acid capable of removing oxides from the base metal. The acid etched base metal proceeds to a water rinse 320 to remove any remaining acid from the base metal and dried 335.

The dried acid etched base metal enters an air lock 340 and vacuum environment. In the vacuum environment, the acid etched base metal can be plasma etched 342 to remove further impurities from the base metal. The plasma etch 342 is an aprotic robust process capable of processing a wide variety of materials. The

plasma etch 342 bombards the base metal with charged particles. The charged particles strike the base metal and "knock off" organic and inorganic impurities from the base metal surface. The plasma etch pre-treatment process 301 could eliminate multiple steps, and associated chemical, recycling and waste treatment costs, from the 5 normal pre-treatment process 201.

A solvent rinse 365 follows the plasma etch 342 to remove dust from the metal surface to be plated. The solvent rinsed base metal can proceed to an electroplating process 370. If the base metal is only slightly greasy and slightly oxidized, it is possible to use the pretreatment process 301 shown in Fig. 3. The parts enter without 10 aqueous pretreatment immediately the airlock 340 and vacuum environment. After plasma etch 342 the parts can proceed to an electroplating process 370 directly or after a rinse in a solvent 365. The plasma etch pretreatment described in Fig. 3 is an aprotic process like the Al-plating and the Mg/Al-plating itself. The whole process with plasma etch as pretreatment and plating is totally aprotic and this means it is 15 100% safe not to introduce hydrogen embrittlement. This is especially important for plating high strength steel for flight sensitive parts.

Electrolyte Formulations

The electrolyte formulations described herein are useful for aluminum, and 20 magnesium/aluminum electroplating. Several factors impact electrolyte development, such as, for example, electrolyte cost, technical and safety concerns, and plating performance.

Cost concerns include, for example, costs of chemicals required during electrolyte lifetime, costs for electrolyte recycling, costs for waste disposal and the 25 electrolyte lifetime.

Technical and safety concerns include, for example, low chemical toxicity, low chemical pyrophoricity, low vapor pressure of the electrolyte solvent at plating temperature and minimal crystallization disturbance.

Plating performance concerns include, for example, high throwing power and 30 covering power, high maximum current density on a part, 100% anodic current efficiency, 100% cathodic current efficiency (forming a pure aluminum layer) and forming a porefree, dense aluminum layer with an appealing visual appearance.

The inventive electrolyte formulations provide improved throwing power and improved current density. In particular, the electrolyte formulations are useful in electroplating base materials with either aluminum or a combination of aluminum and magnesium and the like.

5 Processing

Electroplating may be accomplished with direct current. Direct current provides a current density that is limited since as the current density increases the alkali metal (i.e. potassium, etc.) precipitates together with aluminum on the base metal, which decreases the life of the electrolyte and changes the corrosion resistance 10 of the plating layer on the base metal.

Electroplating may be accomplished at least in part by pulse reverse plating. Pulse reverse plating is a method of electroplating where the electroplating current is periodically reversed. Forward current pulse time can be 30 to 150% of the time required to put one layer of aluminum atoms onto the base metal. Reverse current 15 pulse time can be 1.5 to 5% of the time of the forward current pulse time. Peak reverse current can be 50 to 200 % of peak forward current. Periodic pulse reverse current can increase the effective current forward (effective current density) if the periodic pulse reverse current is optimized. If an electrolyte has $1\text{A}/\text{dm}^2$ maximum current density with direct current, an optimized periodic pulse reverse current can 20 have the following properties:

- forward current : reverse current of 50:2 ms/ms
- peak forward current : peak reverse current ratio of 1:1

The optimized periodic pulse reverse current produced an optimized effective current density of $1.2\text{ A}/\text{dm}^2$. Thus, the optimized periodic pulse reverse current produced an 25 effective plating current density 20% greater than a direct current process.

The optimized periodic pulse reverse plating produces plated base metal with equal to or better physical properties for micro hardness, purity of plated layer, evenness of the plating (throwing power), roughness and visual appearance than the optimized direct current plating.

Aluminum Electroplating Formulations

The inventive electrolyte formulations can include a solvent, a salt, an aluminum alkyl and optional enhancers or additions. The mole ratio of aluminum alkyl to salt may be 2:1.

5 Solvent

The solvent can be any aromatic or aliphatic hydrocarbon such as, for example, benzene, toluene, xylene, meta-xylene, cumene, diphenylmethane, para-isopropyl-methylbenzene, tetralin, ethylbenzene, anisole, dipropylether, diisopropylether, dibutylether, tetrahydrofuran, and the like.

10 Salt for 2:1 Complex

The salt is formed by a cation and an anion. The cation may be an alkali metal, such as, for example, lithium, sodium, potassium, rubidium, caesium and the like or the cation may be a tetrammonium, and the like. The anion may be a halogen, such as, fluoride, chloride, bromide and the like or the anion may be an straight or branched, substituted or unsubstituted alkyl, such as, for example, methyl, ethyl, propyl, butyl, and the like. The anion may also be a hydride.

Al-alkyls for 2:1 Complex

Aluminum alkyls can be illustrated as R^1AlR_2 where R is hydrogen, halogen or a 1-8 carbon straight or branched chain alkyl, such as, for example, methyl, ethyl, 20 n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, and the like and where R^1 is a 1-8 carbon straight or branched chain alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, and the like.

25 Tri-propyl-aluminum (TPA) has a thermal stability that is higher than most other aluminum alkyls. The 2:1 TPA complexes have a high solubility and a high decomposition voltage, which makes TPA a useful component in electrolytes for aluminum plating. High plating temperatures, high concentrations and high maximum current densities can be used with formulations that include TPA.

TPA formulations can be expressed as:



where n is greater than 0 and less than or equal to 2. C is a cation such as, Li, Na, K, Rb, Cs, NR^4 , or mixtures thereof where R' is a C_1-C_8 alkyl, e.g., CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , or mixtures thereof. A is an anion such as, H, F,

Cl, Br, or mixtures thereof. R is H, halogen, or an alkyl such as, CH₃, C₂H₅, C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, or mixtures thereof. The TPA formulation can include a solvent such as, an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof. TPA complex formulations can include solvent and optionally an addition.

5 When n is equal to 0 (no TPA present in complex), the electrolyte includes the 2:1 complex, a solvent and an addition. Additions are described below.

Aluminum and Magnesium/Aluminum Electroplating Formulations

10 The inventive electrolyte formulations can include a solvent, a salt, an aluminum alkyl and optional enhancers or additions. The mole ratio of aluminum alkyl to salt may be 1:1.

Solvent

15 The solvent can be any aromatic or aliphatic hydrocarbon such as, for example, benzene, toluene, xylene, meta-xylene, cumene, diphenylmethane, para-isopropyl-methylbenzene, tetralin, ethylbenzene, anisole, dipropylether, diisopropylether, dibutylether, tetrahydrofuran, and the like.

Cation for 1:1 Complex

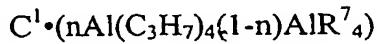
20 The cation may be an alkali metal, such as, for example, lithium, sodium, potassium, rubidium, caesium, magnesium and the like.

Anion for 1:1 Complex

25 The anion may be an aluminum alkyl. Aluminum alkyl anions can be illustrated as AlR⁶₄ where R⁶ is hydrogen or a 1-8 carbon straight or branched chain alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl and the like.

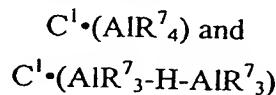
30 Quad-propyl-aluminum (QPA) has a thermal stability that is higher than most other aluminum alkyls. The 1:1 QPA complexes have a high solubility and a high decomposition voltage, which makes QPA a useful component in electrolytes for aluminum and magnesium/aluminum plating. High plating temperatures, high concentrations and high maximum current densities can be used with formulations that include QPA.

QPA formulations can be expressed as:



where n is from 0 to 1. C^1 is a cation such as, Li, Na, K, Rb, Cs, or mixtures thereof. R^7 is H or an alkyl such as, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , or mixtures thereof. The QPA formulation can include a solvent such as, an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof. QPA complex formulations 5 can include solvent and optionally an addition.

QPA formulations can include the following:



or mixtures thereof. C^1 is a cation such as, Li, Na, K, Rb, Cs, or mixtures thereof. R^7 10 is H, or an alkyl such as, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , or mixtures thereof.

When magnesium/aluminum formulations are used, these electrolytes plate aluminum/magnesium alloys onto conductive substrates or base metals using magnesium and aluminum anodes or anodes made out of magnesium/aluminum alloy 15 with the same or similar composition as the desired plating material. Also, these magnesium/aluminum formulations are used to dummy plate with aluminum/magnesium alloy anodes or magnesium anodes to reach the concentration of magnesium alkyls in the electrolyte required for the magnesium/aluminum alloy plating.

20

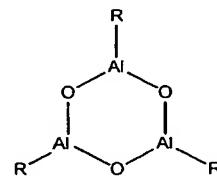
Additions

Aluminum alkyls can be added to the aluminum and magnesium/aluminum formulations defined above including embodiments where n is 0 in an amount in excess of the 2 moles of aluminum alkyl to one mole of salt forming the 2:1 complex. 25 Adding aluminum alkyls in excess can enhance the current density physical property of the formulation. Aluminum alkyls can be illustrated as R^1AlR^2 where R^2 is hydrogen, halogen, or a 1-8 carbon straight or branched chain alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, and the like and R^1 is a 1-8 carbon straight or branched chain alkyl, such as, for 30 example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl, and the like.

Ethers may be added to the formulations, as with aluminum alkyls, to improve the throwing power physical property of the formulation. The ether can be aliphatic

or aromatic. Aliphatic ether may include straight chain or cyclic ethers, for example, dimethylether, ethylene glycol diether, dioxane, tetrahydrofuran, and the like. Aromatic ethers can include, for example, anisole and the like.

Aluminum alkyls may react with trace amounts of oxygen and/or water to 5 form aluminoxanes and/or alkoxy-compounds. These compounds may be provided in the formulation via electrolyte recycle streams. These compounds can enhance the physical properties of the formulation. Alkoxy-compounds can be illustrated as $R^5_pAl(OR^5)_{3-p}$ where p is 0, 1 or 2 and R^5 is a 1-8 carbon straight or branched chain alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, 10 pentyl, hexyl, heptyl, octyl and the like. Alkoxy-aluminum-alkyls may include $R_2^5Al-O-(C_2H_4-O)_q-Al-R_2^5$ or $R_2^5Al-O-(C_2H_4-O)_q-R^5$ or the like where q is 0, 1, 2, 3, or 4. Aluminoxanes can be illustrated as $R^4_2Al-(O-AlR^4_2)_m-OAlR^4_2$ or $(R^4AlO)_n$ where m is an integer from 1-8, n is an integer from 3 to 8, and R^4 is a 1-8 carbon straight or 15 branched chain alkyl, such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, pentyl, hexyl, heptyl, octyl and the like. The compound of the formula $(R^4AlO)_n$ is a ring structured compound; for example, when n is 3 the compound has the structure



20 Particular electrolyte formulations can provide significant advances in current density and throwing power. Some formulations are directed to enhancing throwing power, while others are directed to improving current density or solubility of the complex. Some formulations provide an attractive balance between throwing power and current density. Examples 1 - 4 illustrate useful formulations.

25

Electrolyte Recycling

Several improved electrolyte recycling procedures are outlined below. In the first procedure,

- Take the old/used electrolyte and evaporate a portion of the solvent. A portion 30 of the alkoxy compounds will evaporate with the solvent.

- Cool and crystallize part of the mixture and then separate the alumioxane in the solution and complexes such as crystalline KF*2TEA.
- Use of the complex crystals like KF*2TEA along with some impurities to create new electrolyte. The impurities are important as they simplify the separation process and can be used as addition to the new electrolyte charge.

5 Alternatively,

- Take the old electrolyte and completely evaporate the solvent and the alkoxy compounds.
- Cool and crystallize the mixture.

10 • Dissolve the aluminoxanes with ether or an aliphate (C_5H_{12} to $C_{12}H_{26}$).

- Separate the dissolved aluminoxanes and solid complexes such as KF*2TEA.
- Use the complex like KF*2TEA along with some impurities to create new electrolyte. The impurities are important as they simplify the separation process and can be used as addition to increase solubility and throwing power

15 of the electrolyte.

- Evaporate the remaining ether or the aliphatic solvent on the crystals.
- Add the solvent for the electrolyte and dissolve the complex.

Blower System

20 Fig. 4 is a flow diagram of a blower system for an electroplating process. The blower system 401 includes a blower 410 for forcing gas through the electroplating process 400. The blower 410 provides gas to the electroplating process 400 via an exhaust conduit 450. The gas exits the electroplating process 400 via an exit conduit 460. The gas may pass through a condenser 420. The condenser 420 removes energy

25 from the gas and condenses liquid that can be removed from the blower system 401 via a condensate exit conduit 470 or the condensate can be recycled to the process 400 via a condensate return conduit 480. The gas may be recycled to the blower 410 via a gas recycle conduit 490.

30 The blower system 401 removes volatile electrolyte impurities such as, for example, $AlR_2OC_2H_5$ where R is previously defined. The blower system 401 provides electrolyte bath agitation for the plating process. The blower system 401 provides cooling to the electroplating bath to prevent overheating of the electrolyte during plating. The blower system 401 provides continuous recycling of rinse

solvents such as toluene since the condensate may contain higher concentrations of rinse solvent versus the used outlet rinse bath solution. The outlet rinse bath is the rinse bath used after plating to rinse off electrolyte with the electrolyte solvent from the plated parts.

5 Humidity can be added to the blower system 401 at a humidity intake conduit 430. Humidity may be added to the system prior to opening up the system for maintenance. The liquid can be drained from the electroplating process 400, however pyrophoric material and combustible solvent may remain. Humidity forced through the blower system 401 can destroy this pyrophoric material and the solvent can be
10 condensed and removed from the system 400 before air is admitted into the electroplating process during maintenance. Thus, the blower system 401 can provide an important safety function to the electroplating process 400.

Bulk Plating Device

15 Fig. 5 is a schematic of a bulk plating device 500 for an electroplating process 10 (see Fig. 1). Bulk plating presents unique problems due to the pieces to be plated (bulk) may be many small, large volume pieces. An aluminum plating process will plate only the surface of the base metal (or bulk) near the anode. A high throwing power of the electrolyte is advantageous for maximizing plating rate of bulk pieces.
20 The bulk must be mixed continuously to achieve even plating. An aluminum plating system for bulk plating should have a high average plating rate and a low abrasion rate while plating large amounts of small parts.

25 Sufficient bath agitation results in a minimal diffusion layer around the cathode, which achieves the maximum local current density, for example of 1.3 A/dm² and hence the maximum local plating rate of 0.64 mils per hour. To maximize plating rate, the bulk should be spread out to provide a large surface for aluminum nucleation. The bulk surface to bulk volume ratio should be high. The bulk surface should also maintain a uniform distance to the anode, so that the maximum local plating rate can be achieved over the largest possible area of the bulk surface,
30 resulting in the highest average plating rate.

 Bulk should be mixed carefully with the right tumbling technique to achieve low abrasion rates. If the parts spread out, only slight agitation is necessary to get evenly plated parts. Greater mixing results in better distribution of aluminum on the

bulk or parts. Abrasion and mixing should be carefully balanced to get the required plating uniformity and bath agitation.

Bulk plating may be chosen over rack plating after consideration of several considerations:

- 5 1. Vary large amounts of very small parts can be cheaper to process with a bulk system due to eliminated racking time.
2. It is possible to plate with a bulk system without unplated contact areas on the part to be plated.
3. Bulk plating provides more uniform plating by rotational exposure of the part to the anode.
- 10 4. Holes can be more properly rinsed in the part with bulk plating systems.

Bulk plating can be accomplished with a shaker type bulk plating device 500 shown in Fig. 5. Initially the parts will be fed through the parts entrance 505 into the shaker type bulk plating device 500. The shaker type bulk plating device 500 includes a container chain 510 for conveying bulk 550 into the shaker entrance 560 and for collecting bulk 550 from the shaker exit 570. The container chain 510 can be made of a plurality of containers 511 or other means for transferring bulk 550 from the shaker exit 570 to the shaker entrance 560. The direction of motion of the 20 container chain 510 is shown with arrow 515.

During plating operation, the container chain 510 deposits the bulk 550 into the shaker entrance 560 and collects the bulk 550 from the shaker exit 570 for return to the shaker entrance 560. The electrolyte level 565 may submerge the entire 25 container chain 510 during the plating process. After the bulk 550 is plated, the container chain 510 operations change so that the container chain collects the bulk 550 from the shaker exit 570 and deposits the bulk 550 in the plated parts exit 580. Thus, the container chain 510 will not turn over at the shaker entrance 560 as shown in Fig. 5. The electrolyte level 585 may be lowered below the container chain 510 after the bulk is plated so that a spray rinse 590 can rinse the plated bulk 550 before 30 the plated bulk 550 reaches the plated parts exit 580. The containers 511 are perforated so the rinse 590 liquid can drain to the containers 511 below the top level for increased rinsing as shown in Fig. 5.

The bulk shaker device 500 includes one or more cathodic contact areas 540 that may be a perforated phenolic sheet. The bulk shaker device 500 includes one or more anodes 530. The anodes 530 can be parallel with the cathodic contact areas 540 and may be a sheet. The cathodic contact areas 540 can be between the anodes 530.

5 Screening 520 can be placed around the cathodic contact areas 540 and the anodes 530. The cathodic contact areas 540 and the anodes 530 can be mounted into a frame on wheels that is moving/shaking back and forth with an amplitude shown with arrow 545. The bulk 550 enters the shaker entrance 560 and "shakes" down the cathodic contact areas 540 that may be a perforated phenolic sheet; the bulk 550 may move

10 from a first cathodic contact area 540a to a second cathodic contact areas 540b to a third cathodic contact areas 540c and so on to the shaker exit 570. While on the cathodic contact areas 540 the bulk is plated.

The plating speed of the bulk shaker device 500 may be three times higher than conventional barrel plating systems. The plating time can be 2.25 hours for an

15 average aluminum plate thickness of 0.4 mils for a specific electrolyte with a maximum current density of 1.3 A/dm^2 . The amount of bulk can be 1000 lbs or more.

EXAMPLES

Any of the electrolytes described herein are made using known techniques.

20 The first step is to mix the dry toluene and dry salt with the solvent. Stir and slowly add (under inert gas) the aluminum alkyls. These should be added in order of their reaction heat, with the compound having the lowest reaction heat being added first. For example, add the old electrolyte first, then the dialkylaluminum halogenide, then TPA, then TEA and then TMA. Heat the mixture to 100°C and stir for 5 hours to

25 finish the reaction. After that, the electrolyte is ready for either use or for storage. Note that if impure compounds are used, it may be necessary to perform some dummy plating prior to production in order to remove any impurities present in the electrolyte.

Example 1

30 Table 1 shows electrolyte formulations (A through L) that provide a good balance between throwing power and current density. These formulations are useful for rack plating.

TABLE 1
Al-plating electrolyte
with a good balance between throwing power and maximum current density
values for concentrations in mol per mol salt

Electrolyte	2:1 complex	Salt for 2:1 complex	Cation	Sodium	A	B	C	D	E	F	G	H	I	J	K	L
			Potassium	0.4	1						1	0.2				
			Tetrammonium	1	0.6		0.5	1	0.9		0.8	1			1	1
		Anion	Fluoride			0.5			0.1			0.8	1		0.6	
			Chloride	1	0.6		0.5	1	0.9			0.8	1		0.4	
			Hydride			0.5			0.1			0.8	1		0.6	
		Aluminum alkyls for 2:1 complex	Tri-methyl-aluminum	0.4		0.4	0.5	0.4	0.5	0.4	0.4		1	0.2		0.4
			Tri-ethyl-aluminum			1.6	1.5		1.5		0.4	0.4		1	1	
			Tri-n-propyl-aluminum	1.6	0.4	1.6			1.6		1.5		1	0.7	0.2	
			Tri- <i>iso</i> -butyl-aluminum								1.6	1.6	0.6	0.8	0.9	
			Di- <i>iso</i> -butyl-aluminum-hydride									1.6		0.6	0.8	1.1
		Solvent	Toluene										1	0.2		0.3
			Xylene											0.4		
			Tetraline		4.5									4.1	4.3	5.5
		Additions	Aluminum-alkyls	Tri-methyl-aluminum												
				Tri-ethyl-aluminum	6											
				Tri-n-propyl-aluminum												
				Tri- <i>iso</i> -butyl-aluminum												
				Di- <i>iso</i> -butyl-aluminum-hydride												
				Ethyl-aluminum-di-chloride												
				Ether												
				Ethylene-glycole-di-methyl-ether												
				Di-ethylene-glycole-di-methyl-ether												
				Dioxane												
				Anisole												
		Others	Aluminoxanes													
			R ₂ Al-O-(C ₂ H ₅ O) _n CH ₃													
			R ₂ Al-O-(C ₂ H ₅ O) _n AlR ₂													
			Di-alkyl-alkoxy-aluminum													

Example 2

Table 2 shows electrolyte formulations (M through T) that provides good throwing power. These formulations are useful for barrel or bulk plating.

TABLE 2

Al-plating electrolyte with a good throwing power values for concentrations in mol per mol salt									
Electro- lyte complex	2:1 complex	Salt for 2:1 complex	Cation	Sodium	N	O	P	Q	R
		Anion	Potassium	0.5	0.8	0.9	1	0.9	0.6
			Tetrammonium	0.5	0.5	0.1		0.1	0.4
		Fluoride	Chloride	0.5	0.8	0.9	1	0.9	0.6
			Hydride	0.5	0.5	0.1		0.1	0.4
	Aluminum- alkyls for 2:1 complex	Tri-n-methyl-aluminum	0.5	0.2					
		Tri- <i>n</i> -ethyl-aluminum	1.5	0.9	1.5	0.4	0.5	1	0.2
		Tri- <i>n</i> -propyl-aluminum							0.7
		Tri- <i>is</i> -butyl-aluminum		1.1		1.6		1.5	0.7
		Di- <i>is</i> -butyl-aluminum-hydride						0.6	0.9
	Solvent	Toluene						0.6	0.8
		Xylene		4.2	5.1	5.2		0.6	1.1
		Tetralin						0.3	0.3
Additions	Aluminum- alkyls	Tri-methyl-aluminum						0.4	0.4
		Tri- <i>n</i> -ethyl-aluminum						0.4	0.4
		Tri- <i>n</i> -propyl-aluminum						0.6	0.6
		Tri- <i>is</i> -butyl-aluminum						0.8	0.8
		Di- <i>is</i> -butyl-aluminum-hydride						0.3	0.3
		Ethyl-aluminum-di-chloride						0.3	0.3
	Ether	Ethylene-glycole-di-methyl-ether						0.3	0.3
		Di-ethylene-glycole-di-methyl-ether						0.2	0.2
		Dioxane						0.3	0.3
		Anisole						0.4	0.4
	Others	Aluminoxanes						0.1	0.1
		$R_2Al-O-(C_2H_5-O)_n-CH_3$	0.2	0.2					
		$R_2Al-O-(C_2H_5-O)_n-AlR_3$						0.2	0.2
		Di-alkyl-alkoxy-aluminum						0.3	0.3

Example 3

Table 3 shows electrolyte formulations (U through CC) that provides high current density. These formulations provide fast plating via high current density and are useful for continuous plating and the purification of aluminum.

TABLE 3

		Al-plating electrolyte with a high maximum current density values for concentrations in mol per mol salt									
		U	V	W	X	Y	Z	AA	BB	CC	
Electro- lyte	2:1 complex	Salt for 2:1 complex	Cation Sodium Potassium	0.7	0.7	0.7	1	0.7	1	0.2	1
			Tetrammonium	1	0.3	0.3	0.3	0.3	1	0.8	
		Anion	Fluoride	1	0.7	0.7	1	0.7	1	0.8	
			Chloride	0.3	0.3	0.3	0.3	0.3	1	0.8	
			Hydride								
		Aluminum	Tri-methyl-aluminum	0.2							
			Tri-ethyl-aluminum	0.3	0.3	0.3	0.3	0.3	0.3	0.3	1
			Tri-n-propyl-aluminum	1.5	1.7	1.7	1.7	1.7	1.7	0.8	0.4
			Tri-iso-butyl-aluminum								
			Di-iso-butyl-aluminum-hydride								
		Solvent	Toluene	4	3.8	4.1	4.1	4.1	4.5	3	3.4
			Xylene								
			Tetraline								
		Additions	Aluminum- alkyls	Tri-methyl-aluminum							
				Tri-ethyl-aluminum	0.3	0.5	0.5	0.4	0.4	0.4	0.2
				Tri-n-propyl-aluminum	0.3				0.1	0.1	0.4
				Tri-iso-butyl-aluminum				0.1			
				Di-iso-butyl-aluminum-hydride				0.2			
				Ethyl-aluminum-di-chloride							
				Ether	0.1						
				Ethylene-glycole-di-methyl-ether				0.4			
				Di-ethylene-glycole-di-methyl-ether					0.2		
				Dioxane							
				Anisole	0.5					0.3	
		Others	Aluminoxanes								
			R ₂ Al-O-(C ₂ H ₅ O) _n CH ₃	0.3					0.35	0.3	
			R ₂ Al-O-(C ₂ H ₅ O) _n AlR ₂				0.25			0.2	
			Di-alkyl-alkoxy-aluminum								

In these formulations, an excess of aluminum alkyl provides higher current densities but also provides for a rougher precipitation (Al-layer) and lower throwing power. Anisol or other ethers; alkoxy compounds such as, for example; $R_2^5Al-O-(C_2H_4-O)_q-Al-R_2^5$ or $R_2^5Al-O-(C_2H_4-O)_q-R^5$ where q and R^5 is previously defined; 5 aluminoxanes; dialkylaluminum halogenide compounds can be used to combat these negative effects. These formulations result in a maximum current density that is increased by more than 100 % compared with the values achieved with a specific electrolyte with a maximum current density of 1.3 A/dm².

10 Example 4

The next set of formulations describe a magnesium/aluminum electroplating electrolyte that provides high current density. It has been found that an improved electrolyte can be developed by replacing QEA as the main aluminum alkyl with another aluminum alkyl like QPA, QMA, QiBA or mixtures thereof. Preferred 15 formulations (DD through MM) are provided in Table 4 below.

TABLE 4

Electrolyte	Complex	Cation	Al and Mg/Al-plating electrolyte values for concentrations in mol per mol cation									
			DD	EE	FF	GG	HH	II	JJ	KK	LL	MM
Anion	Sodium		0.1	0.2	0.09	0.12	0.2	0.2	1	1	1	1
	Potassium		0.9	0.8	0.91	0.88	0.8	0.8				
	$(Al(CH_3)_4)^-$			0.2								
	$(Al(C_2H_5)_4)^-$		0.4	0.3	0.4	0.4	0.3	0.2				0.1
	$(Al(C_3H_7)_4)^-$		0.6	0.5	0.5	0.6	0.5	0.4				
	$(Al(C_4H_9)_4)^-$			0.1				0.4				
	$(AlR(H(C_4H_9)_2)^-$						0.2					
	$((CH_3)_3Al-H-Al(CH_3)_3)^-$											
	$((C_2H_5)_3Al-H-Al(C_2H_5)_3)^-$											0.1
	$((C_3H_7)_3Al-H-Al(C_3H_7)_3)^-$											0.2
Solvent	$((C_4H_9)_3Al-H-Al(C_4H_9)_3)^-$											0.9
	Toluene		5.5	6.5	6	5.3	6.5	5.5	2.8	3		0.26
	Xylene											
Additions	Tetraline											4.1
	Aluminum-Alkyls	Tri-methyl-aluminum		0.4								5.4
		Tri-ethyl-aluminum	0.7	0.6	0.8	0.7	0.6	0.4				0.2
		Tri-n-propyl-aluminum	1.4	1	1	1.4	1	0.8	0.67	0.36	0.2	1.8
		Tri-iso-butyl-aluminum			0.2			0.8				0.26
		Di-isobutyl-aluminum-hydride					0.4					
	Ether	Ethylene-glycole-di-methyl-ether										
		Di-ethylene-glycole-di-methyl-ether		0.2								
		Dioxane										
		Anisole										
Others	Aluminoxanes											
	$R_2Al-O-(C_2H_5O)_nCH_3$											
	$R_2Al-O-(C_2H_5O)_nAlR_3$											0.1
	Di-allyl-alkoxy-aluminum											0.1

These formulations employ TPA, TIBA and/or TMA as the main compound, rather than TEA. We have found that this results in a higher throwing power and a higher current density.

We Claim:

1. An electroplating composition comprising:

CA•(nAl(C₃H₇)₃(2-n)AlR₃)

5 wherein:

n is greater than 0 and less than or equal to 2;

C is Li, Na, K, Rb, Cs, NR', or mixtures thereof wherein R' is a C₁-C₈ alkyl or mixtures thereof;

A is H, F, Cl, Br, or mixtures thereof;

10 R is H, halogen, a C₁-C₈ alkyl or mixtures thereof; and

an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof.

2. The composition according to claim 1, wherein C is Na, K, NR', or mixtures thereof.

15

3. The composition according to claim 1, wherein A is F.

4. The composition according to claim 1, wherein A is Cl.

20 5. The composition according to claim 3, wherein C is Li, Na, K, Rb, Cs, or mixtures thereof.

6. The composition according to claim 4, wherein C is NR'.

25 7. The composition according to claim 1, wherein the aromatic hydrocarbon is toluene, xylene, tetraline or mixtures thereof.

8. The composition according to claim 1, wherein;

C is 1 M K;

30 A is 1 M F;

n is 1.6;

R is CH₃;

and the aromatic hydrocarbon is tetralin.

9. The composition according to claim 1, wherein;
C is 0.6 M K and 0.4 M tetraalkylammonium;
A is 0.6 M F and 0.4 M Cl;
5 n is 0.6;
R is C₂H₅ and di-iso-butyl hydride;
and the aromatic hydrocarbon is toluene.

10. The composition according to claim 1, wherein;
10 C is 1 M Na;
A is 1 M H;
n is 1.1;
R is C₂H₅;
and the aromatic hydrocarbon is toluene.

15
11. An electroplating composition comprising:
(a) CA·(nAl(C₃H₇)₃ (2-n) AlR₃) wherein:
n is 0 to 2;
C is Li, Na, K, Rb, C₅, NR₄, or mixtures thereof, in which R is C₁-C₈
20 alkyl, or mixtures thereof;
A is H, F, Cl, Br or mixtures thereof;
R is H, halogen, C₁-C₈ alkyl, or mixtures thereof;
(b) a member selected from:
(i) an aluminum alkyl compound of the formula R¹AlR₂ wherein R
25 is as defined above and R¹ is a C₁-C₈ alkyl group;
(ii) an ether;
(iii) an alkoxy aluminum compound of the formula R⁵₂Al(OR⁵)_{3-p}
where p is 0, 1 or 2 and R⁵ is a C₁-C₈ alkyl;
(iv) an alkoxy aluminum alkyl compound of the formula R⁵₂Al-O-
30 (C₂H₄O)_q-AlR⁵₂ or R⁵₂ Al-O-(C₂H₄O)_q-R₅, where R⁵ is as
defined above and q is 1, 2, 3 or 4;

(v) an aluminoxane compound of the formula $R^4_2Al-(O-AlR^4_2)_m-OAlR^4_2$ or $(R^4AlO)_n$ where m is an integer from 1-8, n is an integer from 3-8, and R^4 is a C_1-C_8 alkyl;

(vi) and a mixture thereof; and

5 (c) an aromatic hydrocarbon, aliphatic hydrocarbon or mixtures thereof.

12. The composition according to claim 11, wherein (b) is an ether.

13. The composition according to claim 12, wherein the ether is dioxane, anisole, 10 ethylene-glycol-di-methyl-ether, di-ethylene-glycol-dimethyl-ether, or mixtures thereof.

14. The composition according to claim 11, wherein (b) is an aluminum alkyl of the formula R^1AlR_2 .

15

15. The composition according to claim 14, wherein R is CH_3 , C_2H_5 , C_3H_7 , C_4H_9 or mixtures thereof.

20

16. The composition according to claim 15, wherein R is C_3H_7 .

17. The composition according to claim 11, wherein (b) is an aluminoxane of the formula $R^4_2Al(-O-AlR^4-)_m-OAlR^4_2$ or $(R^4AlO)_n$ wherein m is an integer from 1-8 and R^4 is C_1-C_8 alkyl, and n is an integer from 3 to 8.

25

18. The composition according to claim 17, wherein R^4 is CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , or mixtures thereof.

30

19. The composition according to claim 11, wherein (b) is an alkoxy aluminum compound of the formula $R^5_pAl(OR^5)_{3-p}$ wherein p is 0, 1 or 2 and R^5 is C_1-C_8 alkyl or mixtures thereof.

20. The composition according to claim 11, wherein (b) is alkoxy aluminum compound of the formula $R^5_2Al-O-(C_2H_4-O)_qR_5$ or $R_2^5Al-O-(C_2H_4-O)_q-Al-R_2^5$ where q is 1, 2, 3, or 4, and R^5 is C_1-C_8 alkyl, or mixtures thereof.

5 21. The composition according to claim 13, wherein:

(a) C is 0.9M K and 0.1M tetraalkylammonium;

A is 0.9M F and 0.1M Cl;

n is 0;

R is CH_3 and C_2H_5 ;

10 (b) the member is ethylene-glycol-di-methylether; and

(c) the aromatic hydrocarbon is toluene.

22. The composition according to claim 11, wherein:

(a) C is 1M K;

15 A is 1M F;

n is 1.6;

R is CH_3 ;

(b) the member is a mixture of (i) aluminum alkyls, where R and R^1 are C_3H_7 and R^1 is C_2H_5 and R is Cl, and (ii) an ether being ethylene-glycol-di-methylether; and

20 (c) the aromatic hydrocarbon is xylene.

23. The composition according to claim 11, wherein:

(a) C is 0.9M K and 0.1M tetraalkylammonium;

25 A is 0.9M F and 0.1M Cl;

n is 0;

R is CH_3 and C_2H_5 ;

(b) the member is a mixture of (i) an aluminum alkyl where R and R^1 are C_2H_5 ; (ii) the ether is anisole, and (iv) a compound of the formula

30 $R^5_2Al-O-(C_2H_5O)_qCH_3$; and

(c) the aromatic hydrocarbon is toluene.

24. The composition according to claim 11, wherein:

(a) C is 1M K;
A is 1M F;
n is 1.5;
5 R is CH₃ and C₂H₅;
(b) the member is a compound of the formula R⁵₂AlO-(C₂H₅O)_q-CH₃; and
(c) the aromatic hydrocarbon is toluene.

25. The composition according to claim 11, wherein:

10 (a) C is 0.7M K and 0.3M tetraalkylammonium;
A is 0.7M F and 0.3M Cl;
n is 1.7;
R is C₂H₅;
(b) the member is a mixture of (i) aluminum alkyls, where R¹ is C₂H₅ and
15 R is Cl and R¹ and R are C₂H₅, and (ii) an ether being anisole; and
(c) the aromatic hydrocarbon is toluene.

26. The composition according to claim 11, wherein:

20 (a) C is 0.7M K and 0.3M tetraalkylammonium;
A is 0.7M F and 0.3M Cl;
n is 1.7;
R is C₂H₅;
(b) the member is a mixture of (i) aluminum alkyls, where R and R¹ are
25 C₂H₅ and R and R¹ are isobutyl, and (ii) an ether being ethylene-
glycol-di-methylether; and
(c) the aromatic hydrocarbon being toluene.

27. An electroplating composition comprising:

30 C•(nAl(C₃H₇)₄(1-n)AlR₄)
wherein:
n is 0 to 1;
C is Li, Na, K, Rb, Cs, or mixtures thereof;
R is H, a C₁-C₈ alkyl or mixtures thereof; and

an aromatic hydrocarbon, aliphatic hydrocarbon, or mixtures thereof.

28. The composition according to claim 27, further comprising:

$C^1 \cdot (AlR^7_4)$; and

5 $C^1 \cdot (AlR^7_3 \cdot H \cdot AlR^7_3)$

wherein C^1 is a cation such as, Li, Na, K, Rb, Cs, or mixtures thereof and R^7 is H, or a C_1 - C_8 alkyl, or mixtures thereof.

29. The composition according to claim 27, wherein the aromatic hydrocarbon is

10 toluene, xylene, tetraline or mixtures thereof.

30. The composition according to claim 27, further comprising:

a member selected from:

- (i) an aluminum alkyl compound of the formula $R^1 AlR_2$ wherein R is as defined above and R^1 is a C_1 - C_8 alkyl group;
- 15 (ii) an ether;
- (iii) an alkoxy aluminum compound of the formula $R^5_p Al(OR^5)_{3-p}$ where p is 0, 1 or 2 and R^5 is a C_1 - C_8 alkyl;
- (iv) an alkoxy aluminum alkyl compound of the formula $R^5_2 Al-O-(C_2H_4O)_q-AlR^5_2$ or $R^5_2 Al-O-(C_2H_4O)_q-R_5$, where R^5 is as defined above and q is 1, 2, 3 or 4;
- 20 (v) an aluminoxane compound of the formula $R^4_2 Al-(O-AlR^4_2)_m-OAlR^4_2$ or $(R^4 AlO)_n$ where m is an integer from 1-8; n is an integer from 3 to 8; and R^4 is a C_1 - C_8 alkyl;
- 25 (vi) and a mixture thereof.

31. The composition according to claim 30, wherein the member is an ether.

32. The composition according to claim 31, wherein the ether is dioxane, anisole, 30 ethylene-glycol-di-methyl-ether, di-ethylene-glycol-dimethyl-ether, or mixtures thereof.

33. The composition according to claim 30, wherein the member is an aluminum alkyl of the formula R^1AlR_2 .

34. The composition according to claim 33, wherein R is CH_3 , C_2H_5 , C_3H_7 , C_4H_9 ,
5 or mixtures thereof.

35. The composition according to claim 34, wherein R is C_3H_7 .

36. The composition according to claim 30, wherein the member is an
10 aluminoxane of the formula $R^4_2Al(-O-AlR^4)_m-OAlR^4_2$ or $(R^4AlO)_n$ wherein m is an integer from 1-8; n is an integer from 3 to 8; and R^4 is C_1-C_8 alkyl.

37. The composition according to claim 36, wherein R^4 is CH_3 , C_2H_5 , C_3H_7 , C_4H_9 ,
15 or mixtures thereof.

38. The composition according to claim 30, wherein the member is an alkoxy aluminum compound of the formula $R^5_pAl(OR^5)_{3-p}$ wherein p is 0, 1 or 2 and R^5 is C_1-C_8 alkyl or mixtures thereof.

20 39. The composition according to claim 30, wherein the member is an alkoxy aluminum compound of the formula $R^5_2Al-O-(C_2H_4-O)_qR_5$ or $R_2^5Al-O-(C_2H_4-O)_q-Al-R_2^5$ where q is 1, 2, 3, or 4, and R^5 is C_1-C_8 alkyl, or mixtures thereof.

40. The composition according to claim 30, wherein:
25 (a) C is 0.2M Na and 0.8M K;
n is 0.5;
R is CH_3 and C_2H_5 ;

30 (b) the member is a mixture of (i) aluminum alkyls where R and R^1 are each CH_3 , C_2H_5 and C_3H_7 , and (ii) an ether being di-ethylene-glycol-di-methylether; and

(c) the aromatic hydrocarbon is toluene.

41. The composition according to claim 30, wherein:

- (a) C is 0.09M Na and 0.91M K;
n is 0.5;
R is C₂H₅ and C₄H₉;
- 5 (b) the member is a mixture of (i) aluminum alkyls where R and R¹ are each C₂H₅, C₃H₇ and i-C₄-H₉; and
- (c) the aromatic hydrocarbon is toluene.

42. The composition according to claim 30, wherein:

- 10 (a) C is 1M Na;
n is 0.1;
R is each C₂H₅; C₄H₉; H and C₂H₅; H and C₃H₇; and H and C₄H₉;
- (b) the member is a mixture of (i) aluminum alkyls where R and R¹ are each C₂H₅, C₃H₇, and i-C₄H₉; and
- 15 (c) the aromatic hydrocarbon is tetraline.

FIG. 1

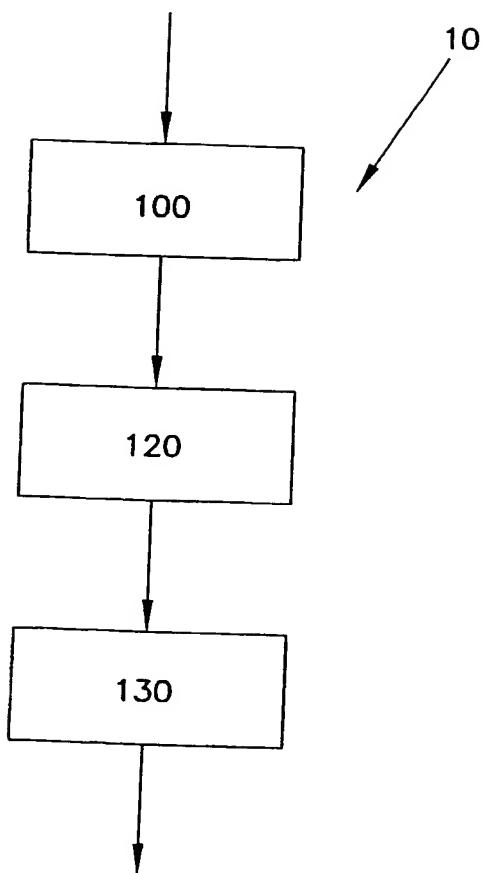


FIG. 2

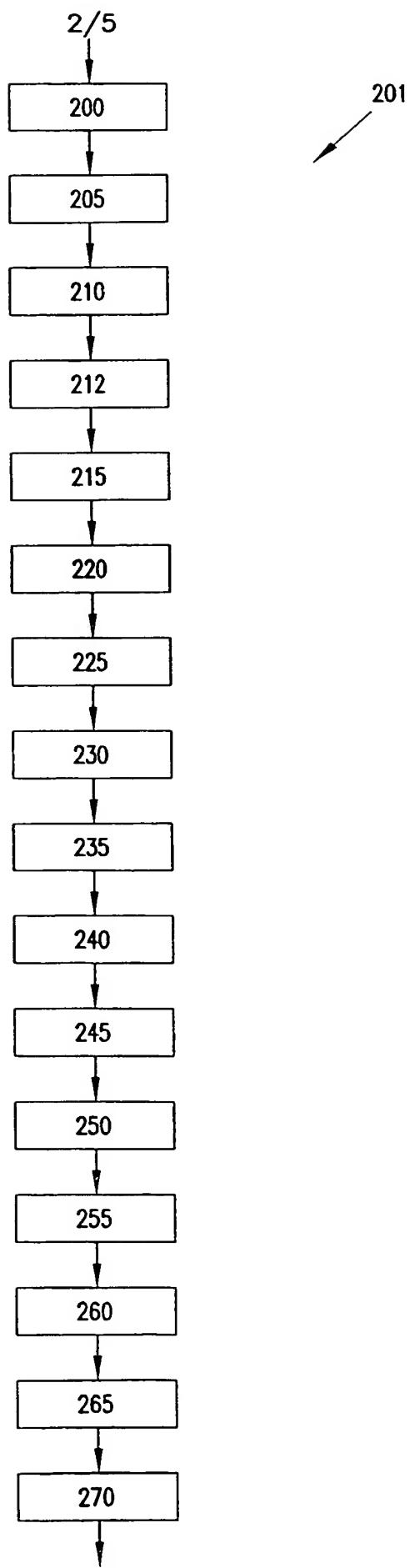
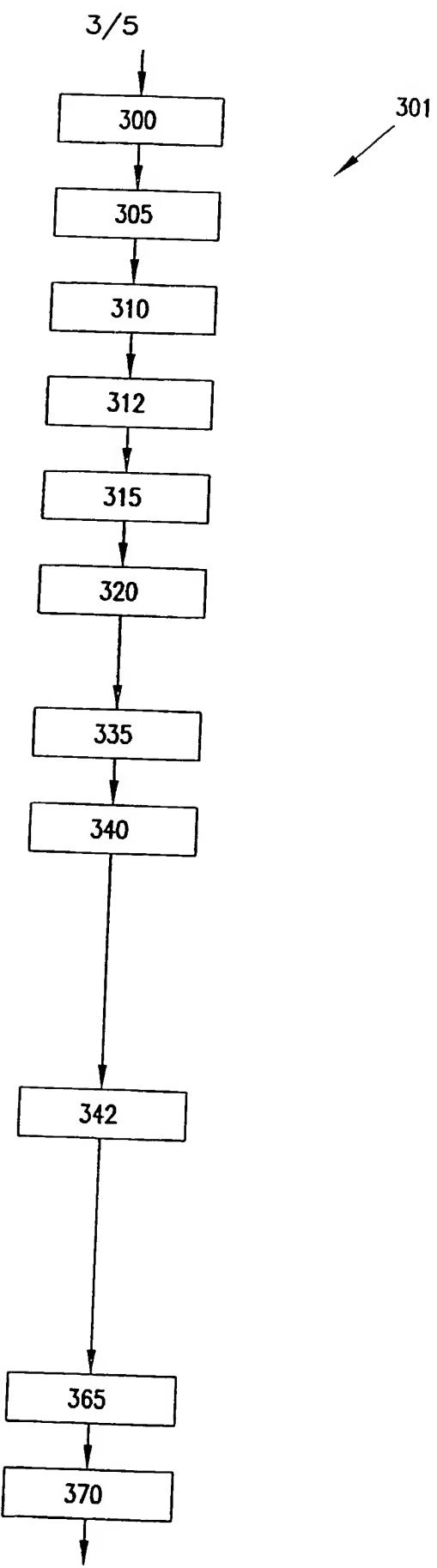
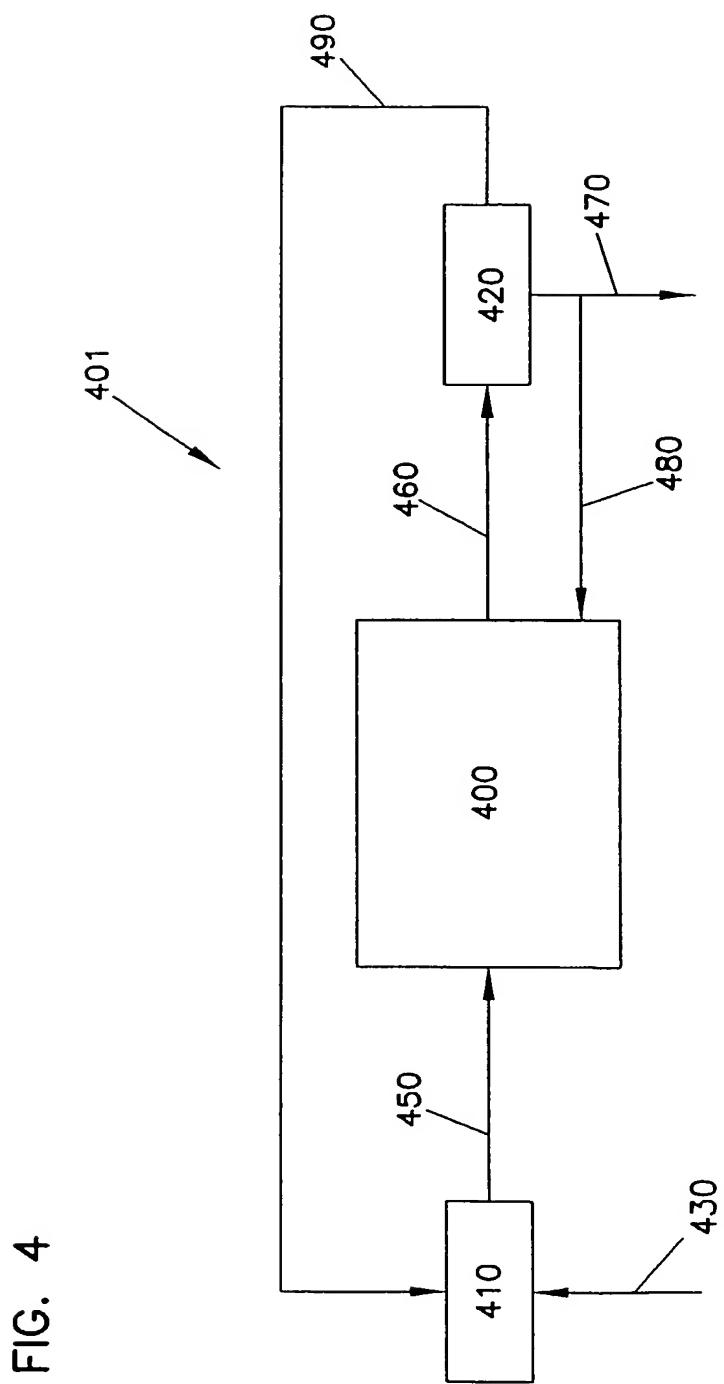
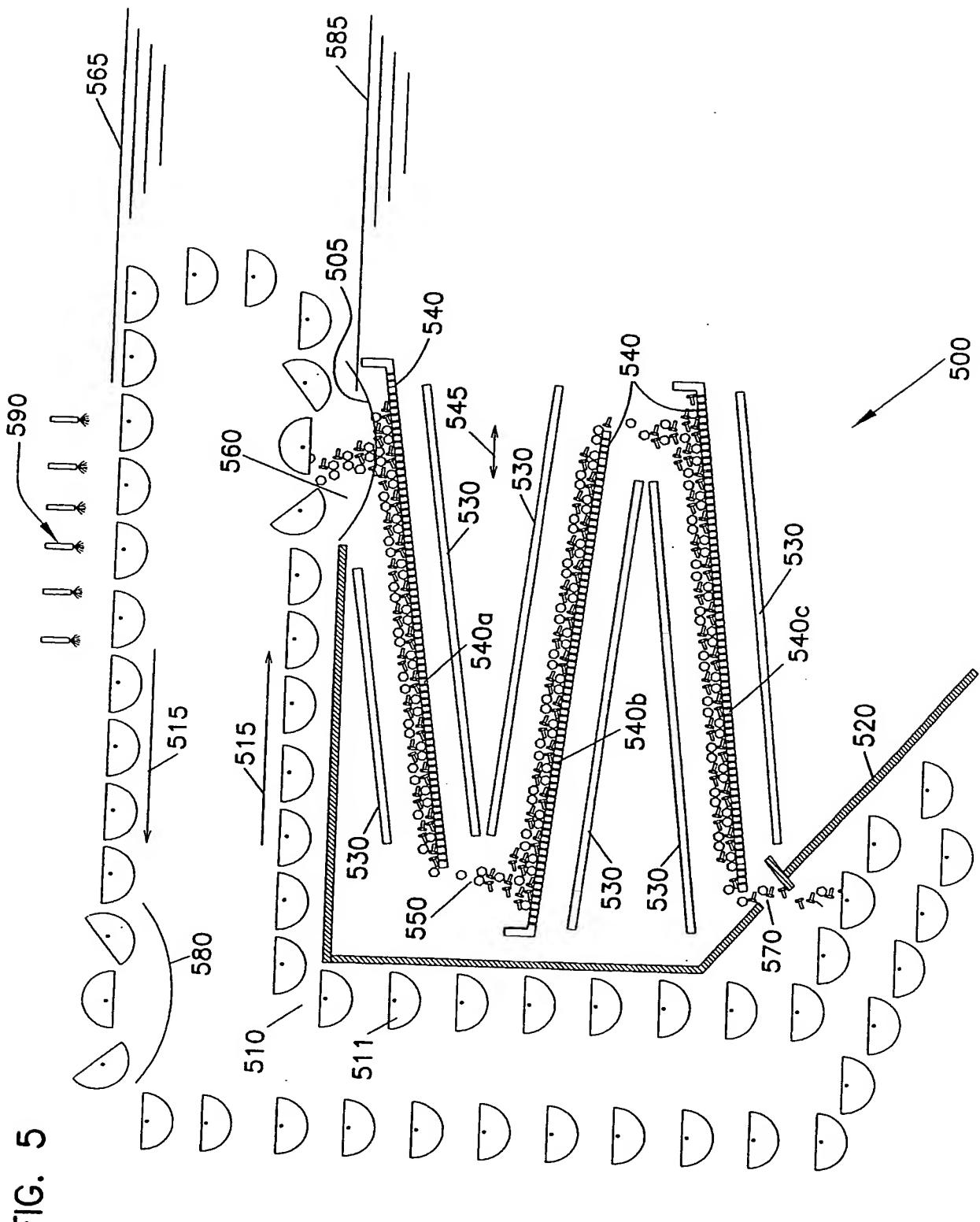


FIG. 3







INTERNATIONAL SEARCH REPORT

Inter SI Application No
PCT/US 02/13832

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25D3/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 207 036 B1 (DE VRIES HANS) 27 March 2001 (2001-03-27)	1-3, 5, 7, 11-16 25
A	claims 1-4, 6 ---	
X	US 4 948 475 A (DOETZER RICHARD ET AL) 14 August 1990 (1990-08-14)	1-5, 7
A	column 2, paragraph 2 claims 1, 5 ---	6
X	WO 98 23795 A (ALCOTEC BESCHICHTUNGSSANLAGEN G ; VRIES HANS DE (NL)) 4 June 1998 (1998-06-04) example 1 ---	11, 12 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *&* document member of the same patent family

Date of the actual completion of the international search

19 September 2002

Date of mailing of the international search report

26/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zech, N

INTERNATIONAL SEARCH REPORT

Inter al Application No
PCT/US 02/13832

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 417 954 A (BIRKLE SIEGFRIED ET AL) 29 November 1983 (1983-11-29) column 1, line 41-68 column 3, line 1-30 ---	1-3, 5, 7, 11
X	DE 198 55 666 A (STUDIENGESELLSCHAFT KOHLE MBH) 8 June 2000 (2000-06-08) claims 1,2,7 examples ---	27-30, 33, 34
A	EP 0 505 886 A (SIEMENS AG) 30 September 1992 (1992-09-30) column 1, line 44 -column 2, line 3 column 3, line 16 -column 4, line 14 claims 1-3 ---	6
A	US 3 234 114 A (KARL ZIEGLER ET AL) 8 February 1966 (1966-02-08) column 3, line 1-16 claims 1-4 -----	19, 20, 38, 39

INTERNATIONAL SEARCH REPORT

1. International application No.
PCT/US 02/13832

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 02 13832

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-10

Electrolyte of $Al(C_3H_7)_3$ with at least 2:1 Aluminiumalkyl : Salt complex.

Furthermore, the salt is composed of Li, Na, K, Rb, Cs or NR^4 and A, F, Cl or Br; the solvent is an aromatic or an aliphatic hydrocarbon.

2. Claims: 11-26

Electrolyte of AlR_3 with at least 2:1 (Aluminiumalkyl : Salt) complex; and an additional component chosen from $R'AlR_2$, ether, alkoxy aluminium compound, alkoxy aluminium alkyl compound, aluminoxane.

Furthermore, the salt is composed of Li, Na, K, Rb, Cs or NR^4 and A, F, Cl or Br; the solvent is an aromatic or an aliphatic hydrocarbon.

3. Claims: 27-42

Electrolyte of AlR_4 with at least 1:1 (Aluminiumalkyl anion : cation) complex.

Furthermore, the cation is one of Li, Na, K, Rb, Cs or NR^4 ; the solvent is an aromatic or an aliphatic hydrocarbon.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 02/13832

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 6207036	B1	27-03-2001	DE AT AU DE WO EP JP ZA	19716495 C1 209264 T 7643598 A 59802731 D1 9848082 A1 0975823 A1 2001521582 T 9803273 A	20-05-1998 15-12-2001 13-11-1998 21-02-2002 29-10-1998 02-02-2000 06-11-2001 27-10-1998
US 4948475	A	14-08-1990	EP JP	0309831 A1 1129989 A	05-04-1989 23-05-1989
WO 9823795	A	04-06-1998	DE AU WO EP JP	19649000 C1 5320098 A 9823795 A2 0948670 A2 2001505253 T	13-08-1998 22-06-1998 04-06-1998 13-10-1999 17-04-2001
US 4417954	A	29-11-1983	DE AT CA DE DK EP ES ES JP JP JP	3202265 A1 20252 T 1209157 A1 3363841 D1 25183 A ,B , 0084816 A2 519248 D0 8403490 A1 1359037 C 58171591 A 61022038 B	28-07-1983 15-06-1986 05-08-1986 10-07-1986 26-07-1983 03-08-1983 16-03-1984 16-06-1984 13-01-1987 08-10-1983 29-05-1986
DE 19855666	A	08-06-2000	DE AT DE WO EP	19855666 A1 220129 T 59901980 D1 0032847 A2 1141447 A2	08-06-2000 15-07-2002 08-08-2002 08-06-2000 10-10-2001
EP 0505886	A	30-09-1992	EP	0505886 A1	30-09-1992
US 3234114	A	08-02-1966	DE GB	1146258 B 961373 A	28-03-1963 17-06-1964

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